

SCIENCE FOR CERAMIC PRODUCTION

UDC 666.3.022:666.321:546.72.002.637

IDENTIFICATION OF IRON COMPOUNDS IN CLAY-CONTAINING MATERIALS

G. N. Maslennikova,¹ R. A. Khalilullova,¹ and Yu. T. Platov¹*Translated from Steklo i Keramika, No. 2, pp. 12–15, February, 1999.*

The discrete thermomagnetic analysis allows identification of the mineral composition of free iron compounds: goethite and hematite (as a consequence of heating in a reducing medium), iron carbonate and siderite (as a consequence of heating in an oxidizing medium). Informative new criteria are used: the reducing and the oxidizing capacity of free iron compounds. A classification of clay-containing materials used in the ceramic industry is proposed consisting of three groups graded according to the reducing capacity of free iron compounds.

It is known that natural deposits of kaolin and other clay-bearing materials with a low iron oxide content are limited. The traditional methods used in concentration of the initial components for ceramic mixtures do not always allow for the required degree of iron removal. In this context, the identification of iron compounds in addition to theoretical value has practical value as well, since it makes it possible to substantiate the optimum concentration schemes for ceramic materials.

Iron can exist in clay-bearing materials in different forms: silicate (isomorphic silicate impurities) or free iron compounds (non-silicate). The latter can be represented by mineral particles in various degrees of dispersion or by the iron oxide films on the surface of silicate mineral particles. When free (non-silicate) iron compounds prevail in the composition of clay-bearing materials, they are easier to remove than in the case when iron incorporated in the silicate crystal lattice is predominant. On the other hand, when weakly crystallized and highly disperse particles predominate among the non-silicate iron compounds, it can be expected that the effect of chemical and microbiological actions on the initial components will be more significant than in the case of a material in which large crystallized particles of iron oxides prevail. Another essential factor is that non-silicate iron compounds can include both divalent (carbonate, sulfides) and trivalent (oxides and hydroxides) iron ions.

The presence of a particular type of iron-containing mineral determines the redox conditions required for its destruc-

tion. Moreover, it should be taken into consideration that when the magnetic concentration method is used, highly magnetic particles are easier to remove than weakly magnetic particles.

The analytical methods used to identify iron-containing minerals include x-ray structural analysis, Mössbauer spectroscopy (nuclear gamma resonance spectroscopy), electron paramagnetic spectroscopy, and magnetic methods [1, 2].

The crystallized iron oxides contained in rocks in significant quantities can be easily identified by Mössbauer spectroscopy and x-ray diffraction analysis [2, 3].

Owing to the low content of iron compounds in the composition of clay-containing materials, their non-stoichiometric composition, and the high dispersion of particles, the use of x-ray structural analysis, nuclear gamma resonance, and electron paramagnetic spectroscopy at room temperature was not effective in identifying these compounds. Traditional magnetic measurements are not acceptable either because of the low magnetic susceptibility of clay-bearing materials, since the iron compounds contained in them are usually weakly magnetic [1, 2].

The methods of chemical identification of iron compounds are relatively simple. Chemical analysis makes it possible to determine both the total iron content and the content of free iron compounds in argillaceous components.

This problem is solved in soil science based on the different solubility of iron compounds using different chemical agents. Some information on the dissolving power of iron-containing minerals using different chemical agents is provided in the review by Parfitt and Childs [4].

¹ State Management Academy; Moscow State University of Commerce; G. V. Plekhanov Russian Economics Academy, Moscow, Russia.

However, the methods developed by soil scientists cannot be used for identification of iron compounds in ceramic materials since the range of the iron compounds in soils is based on the excess of dithionite-soluble iron compared to oxalate iron: $Fe_d > Fe_o$. The analysis of Prosyantovskoe clay revealed the reverse inequality: $Fe_d < Fe_o$ [5]. This result was supported by a study of Australian kaolins [6].

Yu. N. Vodyanitskii suggested using discrete thermomagnetic analysis [7] for identification of iron-containing minerals in soil (goethite α -FeOOH, hematite α -Fe₂O₃, lepidocrocite δ -FeOOH, ferrihydrite $5Fe_2O_3 \cdot 9H_2O$, ferroxylite δ -FeOOH). The method is based on conversion of weakly magnetic iron minerals to highly magnetic ones by heating the samples at a fixed temperature in a reducing or an oxidizing medium with subsequent cooling to room temperature and measuring the magnetic parameter of the cooled sample.

According to Yu. N. Vodyanitskii, lepidocrocite in an oxidizing medium is dehydroxylated with formation of highly magnetic maghemite γ -Fe₂O₃. Moreover, ferrihydrite is reduced to magnetite Fe₃O₄ due to its high hydration. The Fe(II) compounds, namely, siderite FeCO₃ and pyrite FeS₂, in oxidizing conditions also change into magnetite. At the same time, Fe(II) is partly oxidized to Fe(III). In a reducing medium, goethite, ferroxylite, and hematite are reduced to magnetite Fe₃O₄.

In the course of thermomagnetic analysis, clay-containing samples are fired in a muffle furnace at a fixed temperature (from 200 to 650°C with an interval of 50°C). The reducing medium is formed by adding a small amount of sugar to the investigated sample. After the sample is cooled to room temperature, its magnetic susceptibility is determined. The phase transformations of the iron minerals are accompanied by a substantial increase in the magnetic susceptibility of the samples.

The identification of iron minerals is based on the fact that a number of peaks is registered on the differential temperature curve of the considered samples within the temperature interval of 200 – 650°C. The position of a thermal effect on the temperature scale makes it possible to identify these peaks as a specific trivalent iron oxide or hydroxide which has passed into a highly magnetic form.

Since the temperature interval for reducing the magnetic susceptibility maximum values partly coincides for goethite and hematite (the temperature peak of goethite is within the interval of 375 – 475°C, and that of hematite is within 375 – 550°C), it complicates identification of iron oxides when the peaks are within the temperature interval of 375 – 475°C.

In order to reliably discriminate iron oxides in doubtful cases, an additional operation is required, i.e., isothermal heating of the ceramic material at the temperature of 700°C for 1 h. Next the discrete thermomagnetic analysis of the sample calcined in a reducing medium is performed. The correlation of the two differential curves (initial and calcined sample) in certain cases makes it possible to distinguish

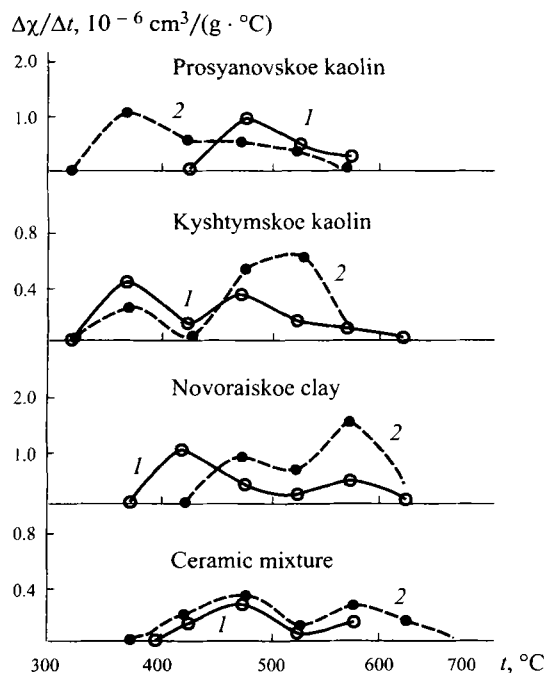


Fig. 1. Differential thermomagnetic curves of ceramic materials: 1) initial sample; 2) calcined sample.

goethite from hematite, since the goethite contribution is absent on the thermomagnetic curve of the calcined sample. The hematite produced by calcination has a lower reducing capacity than goethite. This is manifested by a decrease in the peak height on the secondary curve h_1 as compared to the peak on the primary curve h_0 . Goethite and hematite can be sufficiently reliably distinguished with the ratio of h_1/h_0 . Thus, for goethite $h_1/h_0 < 0.7$, and for hematite $0.7 < h_1/h_0 < 1.3$.

The content of the monomineral iron oxide fraction in clays (solely goethite or solely hematite) can be judged by the level of the reducing capacity RC. This parameter is found from the formula:

$$RC = \chi_{\max} - \chi_0,$$

where χ_0 and χ_{\max} are the values of the initial and the maximum magnetic susceptibility of the samples after heating in a reducing medium.

With a similar formula, the value of the oxidizing capacity of iron carbonates in samples subjected to heat treatment in an oxidizing medium was determined.

The method proved its high efficiency in the analysis of the following clay-bearing materials: raw kaolin from the Zhuravlinyi Log deposit, kaolins from the Kyshtymskoe and the Prosyantovskoe deposits, porcelain rock from the Gusevskoe deposit, and refractory clays [5].

The level of the reducing capacity was used to assess the hematite content in clay-bearing materials. Yu. N. Vodyanitskii proposed the following classification of the reducing

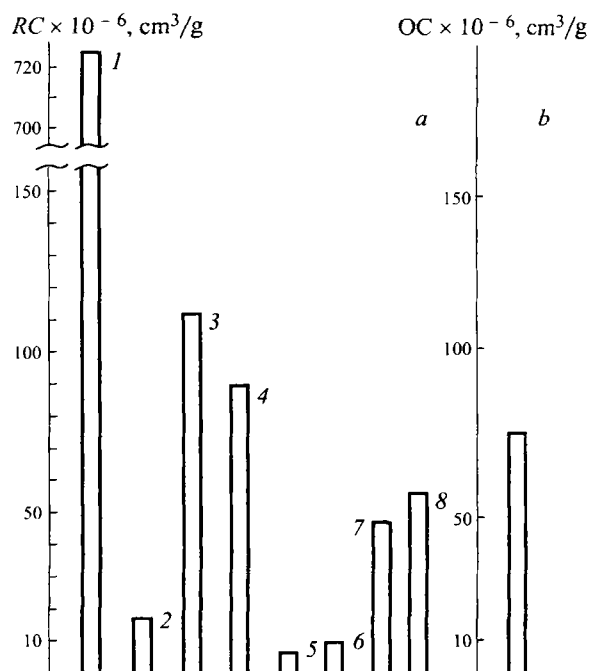


Fig. 2. Reducing capacity RC of ceramic material (a) and oxidizing capacity (OC) of ferruginous Gusevskii rock (b): 1 and 2) ferruginous and low-iron Gusevskii rock; 3) Novoraiskoe clay; 4) Prosyansovskoe kaolin; 5) Zhuravlinyi Log kaolin; 6) Chasov'yarskoe clay; 7) ceramic mixture; 8) Kyshtymskoe kaolin.

capacity of these materials: $RC < 50 \times 10^{-6} \text{ cm}^3/\text{g}$ as low; $50 \times 10^{-6} < RC < 100$ as medium; and $RC > 100 \times 10^{-6} \text{ cm}^3/\text{g}$ as high reducing capacity.

The data shown in Fig. 1 and Table 1 indicate that the only peak registered on the Prosyansovskoe kaolin primary curve at the maximum temperature of 475°C can belong either to goethite or to hematite. It is the height of the secondary curve peak that is significant for identification of the oxide type. A ratio of h_1/h_0 equal to 1.0 indicates that hematite is the main iron oxide in the Prosyansovskoe clay. According

TABLE 1

Material	Total content of Fe_2O_3 , %	$RC \times 10^{-6} \text{ cm}^3/\text{g}$	Iron minerals
Kaolin:			
Prosyansovskoe	0.81	90	Hematite
Kyshtymskoe	1.68	66	Hematite, goethite
Zhuravlinyi Log deposit	0.45	8	Not identified*
Novoraiskoe clay	1.37	112	Hematite
Gusevskii porcelain rock:			
sample 1	2.15	725	Goethite, siderite
sample 1	0.27	17	Not identified
Ceramic mixture	0.45	45	Hematite

* The content of iron oxides in the sample is below the identification limit.

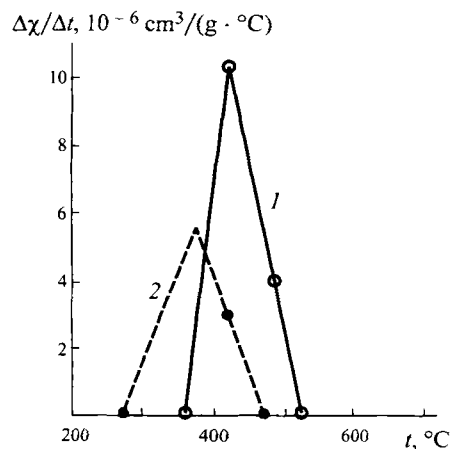


Fig. 3. Differential thermomagnetic curves of porcelain rock from the Gusevskii deposit: 1) initial sample; 2) calcined sample.

to the above classification, its reducing capacity, estimated at $RC = 90 \times 10^{-6} \text{ cm}^3/\text{g}$, corresponds to the medium grade. Two peaks at the maximum temperatures of 375 and 475°C are registered on the primary thermomagnetic curve of Kyshtymskoe kaolin. Both peaks belong to the temperature region in which the peaks of both goethite and hematite can be found. Therefore, it is the second curve that is significant for identification of the iron oxides. Two peaks at the maximum temperatures of 375 and 525°C are registered on the latter curve. The first peak exhibits a decrease in height compared to the first curve ($h_1/h_0 = 0.61$), which is typical of goethite. The height of the second peak, on the contrary, increases: $h_1/h_0 = 1.65$, which is typical of hematite. These data suggest that goethite and hematite coexist in Kyshtymskoe kaolin. The presence of goethite points to the efficiency of magnetic separation in removal of iron from kaolin material, since owing to the crystallographic difference, the goethite particles are weakly bound to kaolinite particles.

The primary differential curve of Novoraiskoe clay exhibits a peak at the maximum temperature of 425°C which can be determined by the presence of either goethite, or hematite. The height of the peak of the second curve does not significantly vary: $h_1/h_0 = 0.92$, which points to the presence of hematite. The reducing capacity of hematite is high: $RC = 112 \times 10^{-6} \text{ cm}^3/\text{g}$ (Fig. 2)

The analyzed samples of porcelain rock from the Gusevskii deposit were taken from two different sites: ferruginous rock with a Fe_2O_3 content equal to 2.15% (sample 1) and low-iron rock with a Fe_2O_3 content equal to 0.26% (sample 2).

The primary curve of the ferruginous sample exhibits a peak at the maximum temperature of 475°C which can be attributed to either goethite, or hematite. The height of the peak on the secondary curve increases significantly, resulting in

$h_i/h_0 = 0.53$, which is evidence of the predominance of goethite in the Gusevskii rock. The reducing capacity of goethite is high: $752 \times 10^{-6} \text{ cm}^3/\text{g}$. This ferruginous sample was subjected to heating in an oxidizing medium as well. The high oxidizing capacity: $OC = 71 \times 10^{-6} \text{ cm}^3/\text{g}$ (Fig. 2) points to the presence of siderite FeCO_3 in the sample, which in oxidizing conditions is partly transformed into magnetite. Thus, siderite and goethite were identified in the ferruginous sample of Gusevskii rock. The weak effects observed on the differential thermomagnetic curve of the low-iron sample of Gusevskii rock did not allow identification of the iron oxides. The reducing capacity of this rock is very low: $17 \times 10^{-6} \text{ cm}^3/\text{g}$. Judging from the absence of oxidizing capacity, the sample does not contain siderite.

The ferruginous sample of the porcelain rock was subjected to magnetic separation after which the specific magnetic susceptibility χ_0 of the magnetic fraction and its reducing capacity were determined (Fig. 4). The magnetic susceptibility of the magnetic fraction attained $25 \times 10^{-6} \text{ cm}^3/\text{g}$ against $\chi = 0$ for the nonmagnetic fraction of the low-iron sample. At the same time, the decrease in the reducing capacity from $17 \times 10^{-6} \text{ g/cm}^3$ to $15 \times 10^{-6} \text{ cm}^3/\text{g}$ makes it possible to identify more reliably the mineral composition of iron oxides in the magnetic fraction. It can be assumed that a small amount of highly magnetic oxides (magnetite Fe_3O_4 or maghemite $\gamma\text{-Fe}_2\text{O}_3$) was converted to a magnetic fraction. Thus, magnetic separation makes it possible to identify a negligibly small quantity (below 0.01%) of highly magnetic iron oxides contained in the material, whose presence in a non-concentrated sample is concealed by the diamagnetism of certain minerals.

The data obtained which characterize the iron-containing minerals in the initial material components are shown in Table 1. Considering the content of the iron minerals that have to be extracted from the material, these data make it obvious that a decrease in the reducing capacity of the initial sample corresponds to a decrease in the content of Fe(III) oxides, for example, hematite. The effect of magnetic separation on this material will be low: it can be assumed that the method of microbiological or chemical purification or a combination of them are more adequate for removal of small impurities of low-magnetic iron minerals.

Raw materials which are characterized by a low reducing capacity ($RC < 50 \times 10^{-6} \text{ cm}^3/\text{g}$) can be most suitable for the production of highly white porcelain. The kaolin from the Zhuravlinyi Log deposit and the porcelain rocks from low-iron sites of the Gusevskii deposit satisfy this condition. The material whose iron oxide reducing capacity is medium ($50 \times 10^{-6} < RC < 100 \times 10^{-6} \text{ cm}^3/\text{g}$) has a lower quality. Such capacity is typical of Prosyantovskoe and Kyshtymskoe kaolins. However, the mineral analysis points to an essential distinction in the composition of the iron-containing impuri-

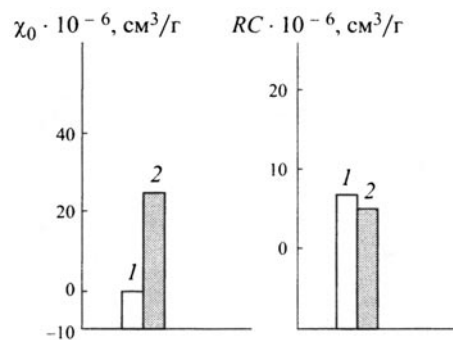


Fig. 4. Specific magnetic susceptibility χ_0 and reducing capacity RC of the initial sample from the low-iron site of the porcelain rock Gusevskii deposit (1) and its magnetic fraction (2).

ties of these kaolins. Thus, Prosyantovskoe kaolin contains hematite, and Kyshtymskoe kaolin contains hematite and goethite. In the second case, magnetic separation can be effective, since goethite is usually not bound as strongly as hematite to the kaolinite particles.

Finally, the third grade of material whose parameter is unfavorable contains a substantial quantity of free iron compounds that have to be removed. According to the research conducted, these materials include Novoraiskoe clay and porcelain rocks from the high-iron sites of the Gusevskii deposit.

Thus, the mineral analysis performed using discrete thermomagnetic analysis makes it possible to identify the clay-bearing material whose free iron-bearing compounds which have to be removed in the course of concentration may have different mineral compositions. In some cases, the analysis data can be used to substantiate the selection of the optimum methods for concentration of the raw material.

REFERENCES

1. Yu. N. Vodyanitskii, *Formation of Iron Oxides in Soil* [in Russian], Moscow (1992).
2. V. F. Babanin, *Forms of Iron Compounds in the Solid Phase of Soils* [in Russian], Author's Abstract of Doctoral Thesis, Moscow (1986).
3. A. I. Ginzburg, *Methods of Mineralogical Studies. Reference Book* [in Russian], Nedra, Moscow (1985).
4. R. L. Parfitt and C. W. Childs, "Estimation of forms of Fe and Al: a review, and analysis of contrasting soils by dissolution and Mossbauer methods," *Austr. J. Soil Res.*, **26**(1), 121–144 (1988).
5. R. I. Khalillulova, *Improvement of Porcelain Whiteness Using Integrated Treatment of Mineral Material* [in Russian], Author's Abstract of Candidate's Thesis, Moscow (1994).
6. S. A. Fysh and J. D. Cashion, "Mossbauer effect studies of iron in kaolin," *Clays Clay Miner.*, **31**(4), 293–297 (1983).
7. Yu. N. Vodyanitskii, "The effect of anthropogenic compression of turf-podzolic soil on iron oxides," *RASKhN*, No. 2, 19–22 (1994).